Cu K-Edge X-ray Fine Structure Changes In CdTe With CdCl$_2$ Processing

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ABSTRACT

We have used the MR-CAT beamline of the Advanced Photon Source at Argonne National Laboratory to study the fine structure in the Cu K-edge x-ray absorption in 3 μm thick polycrystalline films of CdTe on fused silica. 4 nm of evaporated Cu is diffused either with or without prior vapor CdCl$_2$ treatments in dry air. Cu absorption is monitored through the Cu K$_\alpha$ fluorescence using a 13 element Ge detector. The radial distribution function inferred from the absorption fine structure indicates predominantly Cu$_2$Te when Cu is diffused into the as-deposited CdTe film but indicates a Cu$_x$O environment when Cu is diffused *after* the vapor CdCl$_2$ treatment. We believe most of the diffused Cu decorates grain boundaries as oxides, consistent with the low doping densities typically observed in CdTe solar cells. The significance for grain boundary passivation will be discussed.

INTRODUCTION

High performance CdS/CdTe thin film solar cells are usually completed with a low resistance Cu back contact. The copper appears to be critical for achieving heavy p-type doping of the CdTe at the contact. Since CdTe is a material with high electron affinity ($?_A$ = 4.28 eV), a back contact to the p-type CdTe would require a material (usually metal) with a work function of $W = ?_A + E_g \sim 5.78$ eV to achieve flat-band conditions appropriate for hole transport. Since there are no common metals that satisfy this criterion, the second approach is

to fabricate a heavily doped CdTe layer at the back contact to allow for tunneling. Thus essentially all successful stable back contacts to CdTe have involved the use of copper to create a heavily doped layer next to the metal. In our relatively thin (2-2.5 μm CdTe) sputtered cells, we have successfully used very thin evaporated Cu (3 nm) followed by evaporated Au (10-20 nm) to achieve 14% efficiency cells at AM 1.5.[1] If all of the Cu were evenly diffused through the CdTe, one could expect a Cu density of ~10^{20} cm^{-3}. However, C-V measurements of CdTe cells from several laboratories indicate maximum acceptor densities in CdTe of ~5 x 10^{14} cm^{-3}.[2] Thus most of the Cu is inactive. The goal of our measurements was to identify the lattice location of most of the Cu in CdTe.

X-ray absorption fine structure (XAFS) is a powerful technique for understanding the lattice environment around selected elements. The periodic oscillatory structure, known as extended x-ray absorption fine structure (EXAFS), in the absorption spectrum above the edge due to the phase difference between back-scattered and out-going electron waves is the key to this technique. The lattice environments are derivable from absorption spectra by mathematically converting the EXAFS spectrum into a radial distribution function (RDF). [3, 4]

By using the fine structure in the Cu K-edge x-ray absorption spectrum we can elucidate the predominant lattice location of Cu in polycrystalline, thin-film CdTe solar cells. In particular, we have studied how the typical CdCl$_2$ vapor treatment in dry air changes the local environment of the Cu subsequently diffused into CdTe.

High-temperature CdCl$_2$ treatment in the presence of oxygen is a critical step needed to improve the performance of CdTe thin-film cells, which can improve the cell efficiency a factor of two or more. [5, 6] However the process is not yet well understood. The oxygen in the air or He/O$_2$ or Ar/O$_2$ atmospheres during the chloride process is probably active in passivating the grain boundaries although some may also be active in forming doping complexes. Recently, Persson and Zunger [7] have proposed that the key to effective grain

boundary passivation in $CuInSe_2$ is the presence of Cu-vacancy surface reconstruction at the grain boundaries (GBs) of this material which leads to an energy barrier for holes. They suggest that this barrier together with the segregation of impurities to the GBs accounts for the superior performance of polycrystalline CIGS compared with single-crystal material. In the case of CdTe, the present x-ray fine structure measurements suggest that in sputtered cells prepared with post-deposition chloride treatment and with typical amounts of Cu at the back contact, most of the Cu ends up bound with oxygen and resides at grain boundaries.[4] Details are given below. We suggest that this formation of a Cu_2O-like layer at the grain boundaries may play an important role in grain boundary passivation.

EXPERIMENTAL DETAILS

The 2-3 micron CdTe layers were magnetron sputtered at ~ 250 $^{\circ}$C [8] onto either fused silica or Kapton polyimide sheet substrates [9]. All the samples were prepared with 4 to 20 nm evaporated Cu layers which were diffused in N_2 at 150 or 200 $^{\circ}$C for at least 45 minutes. Short etches in 5% hydrochloric acid were also used to remove the metallic copper left on the film surface. (We found that the total x-ray fluorescence signal from a film with a 20 nm deposited and diffused Cu layer typically dropped a factor of two after etching. Thus we estimate that about 10 nm of the Cu diffused into the 3 μm film under the above conditions. This would imply that the average Cu concentration in a typical film is about 0.3 %.) Some of the samples were annealed at 385 $^{\circ}$C in $CdCl_2$ vapor in a dry air environment for 30 minutes before Cu deposition, diffusion and etching. Other samples did not receive the chloride treatment but did receive identical Cu evaporation and diffusion.

XAFS analysis later indicated that the HCl etching was dissolving Cu_2O as well as elemental Cu. Therefore, we also prepared a similar sample with a 2.5 micron CdTe layer and a 4 nm evaporated Cu layer but diffused in flowing N_2 at 200 $^{\circ}$C for 4.5 hours rather than 45 minutes. This sample was not etched.

X-ray Absorption Fine Structure data were obtained at the Materials Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source (Argonne IL) with the system shown in Fig. 1. The Cu K-edge x-ray absorption spectra of the Cu-doped CdTe samples were collected in a fluorescence geometry with a 13-element high purity Ge detector, by setting a 600 eV wide window at the position of Cu K_{α} (8048 eV) in the

Experimental Hutch B
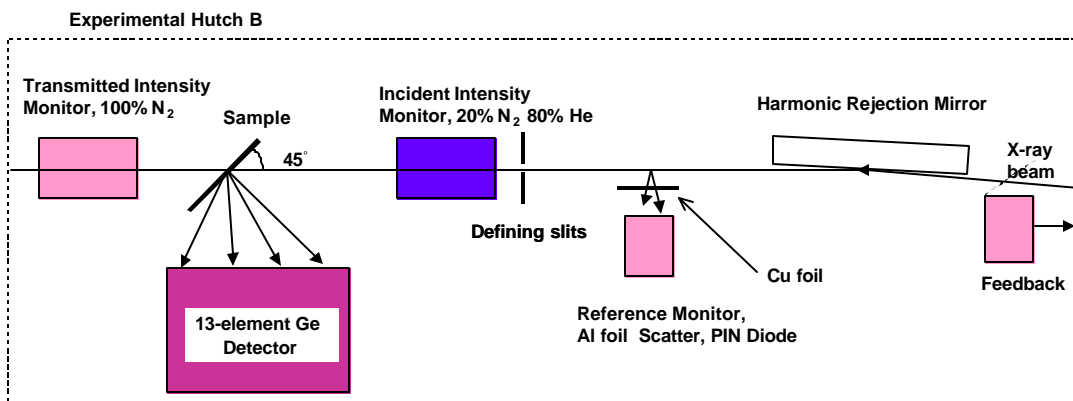
**Fig. 1.** Experimental setup at MR-CAT

fluorescence spectrum, since the copper fluorescence intensity is proportional to the absorption by copper in the thin films. The fluorescence geometry has much better sensitivity than the transmission geometry for ~0.3 % Cu in CdTe because of the high absorption background from the L-shells of Te and Cd near 8 keV. Powdered reference samples of CuO, Cu_2O, $CuCl_2$, CuCl and Cu_2Te powders were applied to the adhesive of several layers of Kapton tapes and the absorption spectra were collected in the transmission geometry with detection by the N_2 ion chamber (Transmitted Intensity Monitor).

RESULTS AND DISCUSSION

The radial distribution functions for the two cases, with and without $CdCl_2$ treatment, are shown in Fig 2. In the copper-diffused but non-chloride treated film, Fig. 2a, we find the RDF closely follows that of a Cu_2Te reference spectrum except for the peak heights. In addition, the first nearest neighbor peak at 2.42 Å shifts to slightly shorter values by about 0.1

Å than for cuprous telluride. We are currently analyzing the data further with an *ab initio* multiple-scattering code FEFF [10] to determine whether this shift is real. The magnitude in the Fourier Transform depends on the coordination number in the corresponding neighbor shell. This is also being studied in further modeling of the XAFS.

For the CdCl$_2$ treated films, the shape of the RDF and the position of the peaks are substantially changed from that of the non-chloride-treated films. Thus, we infer that the chemical environment of the majority of copper atoms is substantially different when diffused after chloride treatment. The peak of the first nearest neighbor resides at a position quite different from that of cuprous telluride, Cu$_2$Te, or of cupric chloride, CuCl$_2$. It also differs from that of CuCl which has similar RDF structure to that of CuCl$_2$ (Fig. 3). However the RDF of the chloride-treated CdTe film corresponds closely to that of cuprous oxide, Cu$_2$O, with the first peak at 1.50 Å, as shown in Fig. 2b. The RDF is not consistent with the existence of bulk Cu$_2$O inclusions in the film since the second nearest neighbors of copper in cuprous oxide are copper atoms.[11] The fact that the second-nearest-neighbor peaks in Fig. 2b, are very different suggests that we are not seeing nanocrystal inclusions of cuprous oxide but rather copper-oxygen pairs formed in the film or quite likely along the grain boundaries.
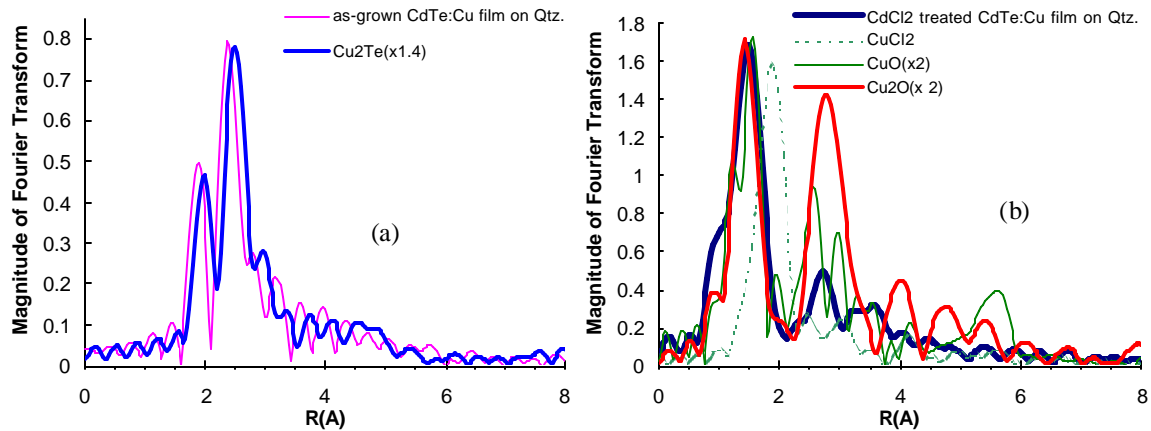
**Fig.2.** Radial Distribution Function (RDF) of Cu diffused CdTe film without (a) and with (b) prior CdCl$_2$ treatment

As a further check we show the RDF of both CuCl and CuCl₂. The RDF of CuCl, Fig. 3, shows a similar bond length and structure to CuCl₂ except for a weaker magnitude of scattering, which is reasonable for the smaller coordination number of copper nearest-neighbors in CuCl. Thus, neither CuCl nor CuCl₂ is found to have similar bond lengths as the CdCl₂-treated CdTe:Cu films.
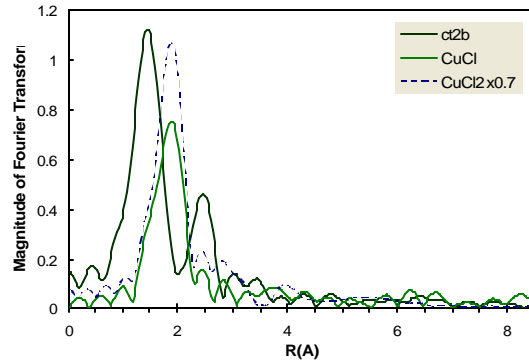
**Fig. 3.** RDF comparison of chloride treated
CdTe: Cu (ct2b) with CuCl and CuCl₂

These x-ray absorption fine structure measurements indicate that films which received the Cu diffusion having no prior treatment with CdCl₂ have the Cu mostly bound with Te similar to Cu₂Te. (Copper telluride compounds have also been identified occurring as interfacial back contact layers. [12]) *However*, if the film has received the CdCl₂ treatment, *which for CdTe cells is always done in the presence of some O₂*, then the Cu appears to be bound not with Cl but with O.
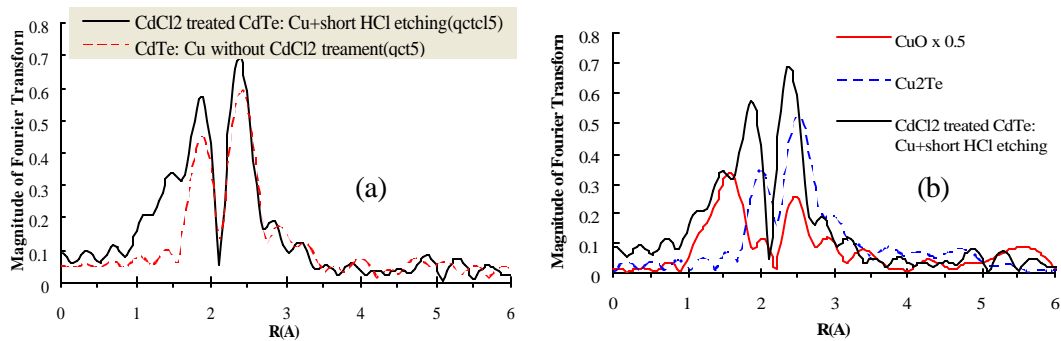
Fig. 4. RDF structures for CdTe: Cu with prior chloride treatment and non-treated CdTe: Cu
(a); CuO and Cu₂Te survived after HCl etching (b)

A PROPOSED MODEL

We believe that the most plausible structure that can explain the above observations is one which has the grain surfaces as the major repository of copper, with the copper bound in a nearest neighbor environment very similar to that of Cu in Cu_2O. A straightforward estimate of the amount of copper available from a 3 nm layer and a 2.5 μm thick CdTe film having ~0.5 μm diameter "cylindrical" grains extending through the film indicates just enough Cu to provide approximately a monolayer coating of the grains.
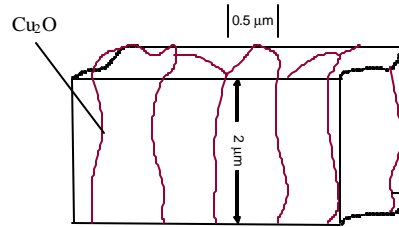
Fig. 5. A model of grain boundaries covered
with Cu_2O in a polycrystalline CdTe film

Additional etching experiments provided an additional consistency check of this model. We found that the XAFS features similar to Cu_2O in the $CdCl_2$-treated CdTe films are removable by selective etching, as shown in Fig 4. After 10 seconds of etching in 9% HCl, the dominant peak at 1.50 Å is gone (cf. Figs. 2 & 3). Post etching, the two major peaks at 1.90 and 2.39 Å in the RDF suggest that most remaining copper is found to be bound with Te as in non-chloride-treated CdTe films, with a small portion of copper bound with O as CuO, yielding the peaks at 1.20 and 1.50 Å. This is consistent with the much faster etch rate of Cu_2O compared with CuO and Cu_2Te in HCl. Concerning the short period of HCl etching which is not more than 10 seconds, we suggest this is evidence that Cu_2O is primarily located along grain boundaries (Fig 5) where it can be dissolved quickly by hydrochloric acid. Furthermore, the fact that the band gap of Cu_2O is 2.0 eV supports the suggestion that this semiconductor may be playing an important role in the passivation of grain boundaries in

CdTe (E_g=1.5 eV) which has received the $CdCl_2$ activation treatment. However, convincing interpretation will need to await information on band line-ups.

As one further check we prepared a sample of $CdCl_2$-treated CdTe film followed by 4.5 hour copper diffusion at 200 ^oC and no acid etching. The radial distribution function (RDF) of this long-time-diffused film confirms that most copper is bound with oxygen as Cu_2O in the CdTe film. This confirms the Cu_2O discovered in our previous chloride-treated CdTe:Cu film resides in the film (e.g., at grain boundaries), instead of arising from metallic copper left on the film surface subsequently oxidized when exposed to air at 200 ^oC.

SUMMARY

These investigations of Cu K-edge X-ray absorption fine structure provide evidence that most copper atoms in CdTe based solar cells are actually oxidized as approximately a monolayer of Cu_2O. Indirect evidence from chloride treatments and HCl etching suggests that this Cu_2O is located at grain boundaries. We propose that this Cu_2O plays an important role in the passivation of grain boundaries leading to an energy barrier for holes, possibly also for electrons, in CdTe which reduces the recombination rate of photo-generated minority carriers. This effective passivation can explain why the relatively small-grain material (0.5 μm or less) produced in magnetron-sputtered (or electrodeposited) CdTe performs almost as well as much larger-grained material from Close Spaced Sublimation (CSS) deposition processes.[13]

ACKNOWLEDGMENTS

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